

**SUPPORTED CATALYST HAVING ELECTRONIC INTERACTION
BETWEEN CATALYTIC PHASE AND SUPPORT MATRIX**

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RELATED APPLICATION INFORMATION

This application is a continuation in part of U.S. Appl. Ser. No. 10/405,008 filed on April 1, 2003 and entitled "Hydrogen Storage Alloys Having A High Porosity Surface Layer"; the disclosure of which is herein incorporated by reference.

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FIELD OF INVENTION

This invention pertains generally to catalytic materials that include a catalytic phase supported on a support matrix. More particularly, this invention pertains to catalytic materials in which supported metal particles interact electronically with a support to provide novel catalytic properties. Most particularly, this invention pertains to customization of catalytic function through the engineering of wavefunction overlap between metal particles and a surrounding support matrix.

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BACKGROUND OF THE INVENTION

20 Chemical reactions underlie many technological and industrial processes and new advances in technology and in mankind's standard of living oftentimes are directly attributable to the discovery of new chemical reactions or improvements in existing chemical reactions. The range of applications that benefit from chemical reactions include pharmaceuticals, petrochemicals,

plastics, lubricants, textiles, and microelectronics. Scientists continually search for new reactions capable of producing new materials and products in new ways.

The feasibility of a particular chemical reaction depends on thermodynamic and kinetic factors. Thermodynamics dictates whether a chemical reaction occurs spontaneously or not.

- 5 According to thermodynamics, spontaneous chemical reactions are those that exhibit a negative Gibbs energy change. Spontaneous chemical reactions are preferred for applications because they are more energy efficient and generally more cost effective than non-spontaneous reactions. Even if a reaction occurs spontaneously, it may still be impractical if it occurs at an insufficient rate. Reaction kinetics govern the rate at which chemical reaction occurs.
- 10 The rate of a chemical reaction typically controls whether a particular reaction is practical or not and much of the effort in the development of chemical reactions is directed toward the goal of increasing the reaction rate. The most common strategy for increasing the rate of a reaction is through the use of a catalyst. A catalyst increases the rate of reaction by providing an alternative, lower energy pathway or mechanism for accomplishing the reaction. Catalysts may be solids,
- 15 liquids or gases and catalyst selection is oftentimes optimized empirically for particular reactions. Identification of an effective catalyst for a particular reaction is frequently not obvious from a simple consideration of the reactant and products involved in the reaction. Instead, detailed experimentation involving a number of potential catalyst materials is normally required for the identification of a suitable catalyst for a particular reaction.
- 20 An important class of existing catalytic materials is the so-called supported catalyst. A supported catalyst consists of a dispersed catalytic phase that is mechanically stabilized on an inert support matrix. The dispersed catalytic phase is typically a metal in the form of small particles (e.g. platinum or nickel) and the support is typically a metal oxide such as alumina or

silica. Supported catalysts are highly effective because the dispersed catalytic phase has a high surface area and the catalytic particles are supported independently in a relatively unaggregated state. Although supported catalysts have for many reactions have been discovered, suitable catalysts for many reactions have yet to be discovered and many of the discovered catalysts are 5 only partially effective. In order to extend the range of practical chemical reactions, it is necessary to identify new supported catalytic materials.

SUMMARY OF THE INVENTION

The instant invention presents a new concept in the design of supported catalysts. Heretofore 10 the catalytic function of supported catalysts has been provided by catalytic particles, typically metals, that are attached to a support matrix that is chemically inert and whose role is limited to one of providing mechanical support. The instant invention provides supported catalytic materials in which the support matrix interacts electronically with supported catalytic particles to influence the catalytic properties thereof to provide materials having new catalytic functionality. 15 The electronic interaction between the support and the catalytic particles originates from the overlap of the wavefunctions of electrons associated with the catalytic particles and the support matrix. The wavefunction overlap provides a degree of freedom that may be used to modulate, alter or otherwise modify electron density at or near the surface of the catalytic particles to thereby influence the catalytic performance thereof. Representative materials according to the 20 instant invention include catalytic metal or metal alloy particles supported on a metallic or oxide support matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1. Schematic depictions of a catalytic phase supported by a support matrix.

DETAILED DESCRIPTION OF THE INVENTION

5 Conventional supported catalysts have been widely used to promote a variety of chemical reactions. Conventional supported catalysts include a dispersed catalytic phase that is supported on a support matrix. The role of the support matrix is to provide mechanical support or stabilization of the dispersed catalytic phase. A conventional support is chemically and electronically inert with respect to the catalytic phase and merely provides a surface or structure
10 upon which a catalytic phase can be formed and retained. A common method for preparing a conventional supported catalyst includes dissolving a precursor for the catalytic phase in a solution, depositing the solution on a support and forming the catalytic phase by allowing the solvent of the precursor solution to evaporate. The catalytic phase so formed is dispersed across the surface and pores of the support matrix. The interaction between the support matrix and the
15 catalytic phase in a conventional supported catalyst is physical in nature. The support matrix functions as a substrate for holding or mechanically stabilizing a catalytic phase that is formed thereon through evaporation or some other method. The catalytic phase is akin to a layer, which is potentially heterogeneous and/or non-uniform, that conformally rests on the support. The catalytic properties of a conventional supported catalytic material are those that are intrinsic to
20 the catalytic phase. Except for providing mechanical stabilization, dispersion and inhibiting aggregation, the support matrix has little or no influence on the catalytic properties of the catalytic phase. The support matrix of a conventional supported catalyst is thus referred to herein as an inert or electronically inert support matrix.

The catalytic phase of conventional supported catalysts is typically comprised of particles of a catalytic material. The beneficial properties of conventional supported catalytic materials accrue from the intrinsic catalytic properties of the catalytic phase in combination with the dispersed physical positioning provided by the inert support of the catalytic particles that comprise the 5 catalytic phase. Dispersal of the catalytic phase prevents or inhibits aggregation of catalytic particles and improves catalytic performance by providing a high surface area for chemical reaction.

The instant invention is directed at creating next generation supported catalytic materials that have improved and/or heretofore unattainable catalytic performance. The instant invention 10 provides a new degree of freedom in the design of supported catalytic materials to provide a new class of catalysts whose functionality extends beyond that of conventional supported catalytic materials. The instant catalytic materials are supported catalytic materials that include a catalytic phase and a support matrix where the support matrix provides more than simple mechanical stabilization and physical dispersion of the catalytic phase. In the instant materials, the support 15 matrix also interacts electronically with the catalytic phase to provide a mechanism for altering, enhancing or otherwise modifying the intrinsic catalytic properties of the catalytic phase. In the instant invention, an electronic interaction between the catalytic phase and support matrix is present and acts to modify the catalytic properties of the catalytic phase relative to a corresponding catalytic material that includes the catalytic phase supported by an electronically 20 inert support matrix. The support matrix of the instant invention may hereinafter be referred to as an electronically active support matrix.

The catalytic phase of the instant materials is preferably a metal or metal alloy in the form of particles. The catalytic particles have a particle size distribution that is typically non-uniform and

the catalytic particles are dispersed on the support matrix according to a spatial distribution. For a given particle size distribution and spatial distribution of catalytic particles on a support matrix, the electronic interaction between the catalytic particles and an electronically active support matrix provides for improved catalytic properties of the catalytic particles having the same
5 particle size distribution and spatial distribution when supported by an inert support matrix. The electronic interaction of the instant invention may additionally create size and/or spatial distributions of catalytic particles not achievable on inert support matrices.

As in conventional supported catalysts, size influences the intrinsic catalytic properties of the catalytic particles. Smaller particles sizes provide higher surface area to volume ratios and are
10 accordingly preferred since high surface areas promote catalytic activity. Sufficiently small particle sizes may also place a catalytic material into the quantum limit regime, thereby providing unorthodox structure, bonding and catalytic sites. In addition to surface area and intrinsic catalytic activity, the size of the catalytic particles in the context of the instant invention further influences the tendency of the catalytic phase to interact electronically with a support
15 matrix. As used herein, electronic interaction refers to an interaction between a catalytic phase and an electronically active support matrix that involves a transfer or delocalization of electron density from the catalytic phase to the support matrix or from the support matrix to the catalytic phase or mutual transfer or delocalization between the catalytic phase and the support matrix. As used herein, electronic interaction may also refer to an interaction between a catalytic phase and
20 a support matrix that involves an inhibition or localization of the spatial extent of electron density of the catalytic phase and/or support matrix. As described more fully hereinbelow, the electronic interaction present in the instant materials arises from an overlap of the wavefunctions of electron density associated with the catalytic phase and an electronically active support

matrix, where the overlap can lead to bonding or anti-bonding effects that may influence the electron density in the vicinity of or between the catalytic phase and support matrix. The delocalization or localization of electron density associated with the electronic interaction of the instant materials distinguishes the interaction of the catalytic phase and the support from the 5 Coulombic type electrostatic interaction that may be present in conventional supported catalysts. Whereas a Coulombic type interaction is physical in nature, delocalization or localization of electron density is chemical in nature.

While not wishing to be bound by theory, the instant inventor believes that the electronic interaction between the catalytic phase and electronically active support of the instant materials 10 may be viewed in quantum mechanical terms. The cohesiveness of materials is ultimately due to chemical bonds that form between the atoms that comprise a material. Chemical bonds are essentially regions of electron density that stabilize a collection of atoms. The electrons originate from atomic orbitals on atoms. The atomic orbitals of an atom, frequently in hybridized form, combine with atomic orbitals of neighboring atoms to form bonding and anti-bonding molecular 15 orbitals. The stabilization associated with the occupation of bonding orbitals by electrons drives the formation of bonds and underlies the stability of materials.

In quantum mechanical terms, the electron density associated with atomic and molecular orbitals can be described by wavefunctions and chemical bonding and anti-bonding can be described in terms of combining wavefunctions. The formation of bonding molecular orbitals 20 from atomic orbitals results from the overlapping of the wavefunctions of atomic orbitals to produce new wavefunctions that may extend over multiple atoms. The extended wavefunctions signify the delocalization of electron density from one atom to other atoms in a material. The tendency for the electron density of an atom to delocalize is related to the spatial extent of the

wavefunction that describes the electron density and chemical bonding is related to the degree to which the wavefunction of one atom spatially overlaps the wavefunction of neighboring atoms.

Wavefunctions that extend away from an atom show a greater tendency to overlap wavefunctions of neighboring atoms. Spatially localized wavefunctions, in contrast, show little

- 5 spatial extent and correspond to electron density that is closely held by or tightly bound to an atom. Tightly bound wavefunctions show little tendency to interact with or overlap wavefunctions of neighboring atoms. Electron density described by spatially extended wavefunctions is thus more likely to delocalize than electron density described by tightly bound wavefunctions.

- 10 Multi-electron atoms have multiple occupied atomic orbitals and form multiple molecular orbitals upon forming chemical bonds. Anti-bonding molecular orbitals may also form. The

various atomic orbitals have varying spatial extents and show varying degrees of spatial overlap with atomic orbitals from neighboring atoms. It is generally accepted that the spatial extent of atomic orbitals increases in the following order: $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p \dots$ The

- 15 outermost or valence electrons of an atom are generally the most spatially extended and therefore correspond to electron density having a wavefunction showing the greatest tendency to overlap spatially with wavefunctions from neighboring atoms to form bonding and/or anti-bonding molecular orbitals. Generally speaking, the spatial extent of a wavefunction increases as the energy of the orbital (atomic or molecular) increases. Higher energy electrons within atoms are 20 thus more likely to localize or delocalize through interactions with neighboring atoms than are lower energy electrons.

The electronic interaction between the catalytic phase and electronically active support of the instant materials may be described in terms of an overlap of wavefunctions. The catalytic

particles of the catalytic phase are collections of atoms that are chemically bonded with electron density describable by one or more wavefunctions. The support matrix is similarly a collection of atoms having its own electron density describable by a separate set of wavefunctions. The electronic interaction present in the instant materials corresponds to the development of an 5 overlap between one or more wavefunctions of the catalytic particles and one or more wavefunctions of the support matrix.

The effect of the electronic interaction present between the catalytic particles and support matrix of the instant materials on the catalytic properties depends on the strength and nature of the overlap of wavefunctions. As is known in quantum mechanics, the overlapping of 10 wavefunctions (e.g. superpositions or combinations) may lead to the formation of bonding and/or anti-bonding orbitals. Bonding orbitals typically lead to an increase in electron density in the space between the interacting entities associated with the overlapping wavefunctions. Such a bonding type electronic interaction results in a delocalization of electron density from one or more of the interacting entities to others of the interacting entities or to the space between the 15 interacting entities. In the instant materials, a bonding type electronic interaction due to wavefunction overlap may occur in which electron density delocalizes from one or both of the catalytic phase and support matrix.

It is to be understood in the context of the instant invention that a bonding type electronic interaction need not necessarily imply that a chemical bond forms between the catalytic phase 20 and the support matrix. The attachment of the catalytic phase to the support matrix may remain physical or mechanical in nature in the presence of a bonding type electronic interaction. In this instance, a chemical bond per se may not form. The interaction is viewed as a bonding type of interaction when electron density delocalizes to or from the catalytic phase due to an overlapping

of one or more wavefunctions of the catalytic phase with one or more wavefunctions of the support matrix. In the limit of a sufficiently strong bonding-type electronic interaction, a chemical bond may form between the catalytic phase and the support matrix.

Anti-bonding orbitals formed by overlapping wavefunctions typically lead to a decrease in

5 electron density in the space between the interacting entities associated with the overlapping wavefunctions. Such an anti-bonding type electronic interaction prevents delocalization of electron density to the region between the interacting entities associated with the overlapping wavefunctions. Instead, a repulsive type effect results that leads to a reduction in the spatial extent of electron density emanating from one or both of the catalytic phase and support matrix.

10 Electron density residing in orbitals associated with the catalytic phase and/or support matrix becomes more localized and leads to an increase in electron density in the vicinity of the catalytic phase and/or support matrix relative to a situation in which no anti-bonding electronic interaction is present. In the presence of an anti-bonding type electronic interaction, electron density originally associated with the catalytic phase and/or support matrix becomes denser and

15 more localized.

The catalytic properties of the catalytic phase are largely determined by the distribution of electron density at or near its surface. The catalytic phase of the instant invention is preferentially comprised of particles having catalytic activity where the catalytic activity depends on the electron density at or near the surface of the particles. Catalytic function requires an ability of

20 catalytic particles to attract and stabilize one or more reactant species for a period of time sufficient to permit a chemical reaction or molecular rearrangement to occur. The electron density at or near the surface of the catalytic particles influences the strength of interaction between the catalytic particle and potential reactants as well as factors such as the geometric

position or orientation of a reactant on the surface of the catalytic particles. Catalytic reactions occur at selected sites on the surfaces of catalytic particles. These catalytic sites are catalytically active as a consequence of a favorable distribution of electron density. Effects that alter the distribution of electron density at or near the surface of a catalytic particle influence the catalytic activity.

The electronic interaction present in the instant materials, whether it be of the bonding-type or anti-bonding type, provides a new degree of freedom for modifying the distribution of electron density at or near the surface of the catalytic particles. A bonding-type electronic interaction may lead to a delocalization of electron density away from the surface of a catalytic particle and may result in a decrease in electron density at or near the surface of catalytic particles. An anti-bonding type electronic interaction may lead to a localization of electron density the vicinity of the surface of a catalytic particle and may result in an increase in electron density at or near the surface of the catalytic particles. By modifying the electron density at or near the surface of catalytic particles, the electronic interaction resulting from the wavefunction overlap present between the catalytic particles and support matrix of the instant materials provides a mechanism for modifying the catalytic properties of the catalytic phase and the supported material in general.

The strength and type (bonding vs. anti-bonding) of the electronic interaction in the instant supported catalytic materials ultimately depends on the extent and nature of wavefunction overlap between the catalytic phase and electronically active support matrix. The extent and nature of overlap depend on several factors. First, the spatial extent of the wavefunctions associated with the electron density of the catalytic phase and support matrix influences the extent of overlap. Of particular relevance is the extent to which the wavefunctions contributing

to the overlap extend beyond the physical boundaries of the catalytic phase and support matrix.

Tightly bound electron density is described by wavefunctions that are essentially contained within the boundaries of the aggregate of atoms from which the wavefunctions originate. Such wavefunctions show little tendency to spatially overlap wavefunctions originating from nearby aggregates of atoms. Catalytic phases or support matrices having tightly bound wavefunctions show little tendency to overlap with each other or other wavefunctions and consequently show little tendency to provide the electronic interaction underlying the enhanced catalytic properties of the instant invention.

Catalytic phases or support matrices whose wavefunctions extend beyond the physical boundaries of the aggregate of atoms from which the wavefunctions originate, in contrast, show greater tendency to exhibit the spatial overlap necessary to provide the electronic interaction of the instant invention. Generally speaking, wavefunctions associated with electron density corresponding to higher energy occupied atomic and/or molecular orbitals are more spatially extensive than wavefunctions associated with lower energy orbitals. As orbital energy decreases, electrons on atoms become more tightly bound and interact to a lesser degree with electrons on neighboring atoms. Electrons in higher energy orbitals are oftentimes referred to as valence electrons, while the more tightly bound electrons in lower energy orbitals are oftentimes referred to as inner core electrons.

Factors that influence the spatial extent of wavefunctions include the Lewis basicity of the catalytic phase and/or support matrix and the size of particles in the catalytic phase. Lewis basicity is a measure of the electron donating capability of the catalytic phase and/or support matrix. Greater Lewis base strength of a catalytic phase and/or support matrix composition

increases the likelihood of spatial overlap of wavefunctions and of achieving the electronic interaction of the instant invention.

The size of the particles of a catalytic phase also influences the spatial extent of the wavefunctions originating from the catalytic phase. More specifically, as the particle size 5 decreases, the electron density of the catalytic phase becomes less bound and the resulting wavefunctions become spatially more extended and more likely to overlap with wavefunctions of the support matrix. Due to size considerations, the catalytic phase of the instant materials includes metal or metal alloy particles having a size of 100 Å or less. More preferably, the catalytic phase includes metal or metal alloy particles having a size of 50 Å or less. Most 10 preferably, the catalytic phase includes metal or metal alloy particles having a size of 20 Å or less.

A second factor contributing to the extent and nature of wavefunction overlap is the relative orientation of the interacting wavefunctions of the catalytic phase and support matrix.

Wavefunctions are typically spatially non-isotropic and have characteristic directionality and 15 reflect asymmetries of electron density in bonding and anti-bonding molecular orbitals. Even if wavefunctions show great spatial extent, the regions of space occupied by the wavefunctions of the catalytic phase and support matrix must be co-extensive in order to create spatial overlap and to produce the electronic interaction of the instant invention. The requirement for spatial co-extensiveness is tantamount to a directionality or wavefunction orientation requirement.

20 A third factor contributing to the extent and nature of wavefunction overlap is the relative energy of the interacting wavefunctions of the catalytic phase and support matrix. It is known from quantum mechanics that the relative energies of wavefunctions having adequate spatial extent and suitable orientation influences the strength of interaction between the wavefunctions

- and the resulting effect on electron density. The closer in energy the interacting wavefunctions are, the stronger is their strength of interaction. Wavefunctions having identical or similar energies show stronger interactions than wavefunctions having dissimilar energies. A stronger electronic interaction between wavefunctions indicates a greater degree of mixing of
- 5 wavefunctions from the catalytic phase and the support matrix to provide a new wavefunction that better reflects a combination of the properties of the catalytic phase and support matrix. As the mismatch in energy between contributing wavefunctions increases, mixing may still occur, but the resulting wavefunctions exhibit characteristics that are predominantly controlled by the wavefunctions of one of the catalytic phase or support matrix.
- 10 A fourth factor contributing to the extent and nature of wavefunction overlap is the relative phases of the interacting wavefunctions of the catalytic phase and support matrix. The wavefunction phase can be positive or negative and the relative phases of the wavefunctions of the catalytic phase and support matrix dictates whether the electronic interaction is of the bonding type or anti-bonding type. Wavefunctions having the same phase interact to provide a
- 15 new wavefunction of the bonding type and result in a bonding-type electronic interaction between the catalytic phase and support matrix of the instant invention. Wavefunctions having opposite phase interact to provide a new wavefunction of the anti-bonding type and result in an anti-bonding type electronic interaction between the catalytic phase and support matrix of the instant invention.
- 20 In addition to electronic interactions of the bonding and anti-bonding types, the electronic interaction of the instant materials also includes interactions of the donor-acceptor type. A donor-acceptor interaction is an interaction between orbitals or wavefunctions of the catalytic phase and support matrix in which at least one of the interacting wavefunctions is unoccupied or only partly

occupied and not fully occupied. A donor-acceptor interaction is one in which electron density is transferred from the donor to the acceptor where the acceptor receives the transferred electron density in a partially occupied or unoccupied orbital. In the instant invention, either the catalytic phase or the support matrix may perform as the donor or acceptor. If the catalytic phase 5 functions as the donor, the donor-acceptor interaction leads to a net reduction of electron density in the vicinity of the surface of the catalytic phase and the catalytic properties are accordingly altered. Conversely, if the catalytic phase functions as the acceptor, the donor-acceptor interaction leads to a net increase of electron density in the vicinity of the surface of the catalytic phase.

10 Through the principles of wavefunction overlap, the instant invention provides supported catalytic materials exhibiting an electronic interaction between the catalytic phase and the electronically active support matrix. As described hereinabove, the electronic interaction may be of the bonding, anti-bonding or donor-acceptor type and is manifest in an alteration of the total electron density and/or distribution thereof in the vicinity of the surface or catalytic sites of the 15 particles of the catalytic phase. The alteration is relative to and represents a deviation of the electron density and/or distribution thereof in the vicinity of the surface or catalytic sites of the particles of the catalytic phase when equivalently dispersed on an inert support matrix. The instant electronic interaction is a mutual interaction between the catalytic phase and support matrix and results from the fact that the support matrix provides for more than mere physical 20 dispersion and mechanical support of the catalytic phase.

A schematic depiction of the structure and electronic interaction provided by the instant supported catalytic materials is provided in Figs. 1A – 1C. Fig. 1A shows a depiction of a conventional supported catalytic material. The conventional supported catalyst includes a

particle of a catalytic phase **100** supported by an inert support **200**. The electron density present at or near the surface of the catalytic particle **100** is denoted by Q. Figs. 1B and 1C show depictions of different embodiments of supported catalytic materials according to the instant invention. The material depicted in Fig. 1B includes the particle of the catalytic phase **100** (same 5 particle as shown in Fig. 1A) supported by the electronically active support matrix **300**. The electronically active support matrix **300**, through wavefunction overlap as described hereinabove, provides a net transfer of electron density to or near the surface of the catalytic particle **100**. The direction of transfer of electron density is depicted by the arrow. As a result of the wavefunction overlap, the electron density at or near the surface of the catalytic particle **100** 10 has increased to $Q + \Delta$ where Δ represents the perturbation of electron density at or near the surface of the catalytic particle **100** due to the electronic interaction with the support matrix **300**. The material depicted in Fig. 1C includes the particle of the catalytic phase **100** (same particle as shown in Fig. 1A) supported by the electronically active support matrix **400**. The electronically active support matrix **400**, through wavefunction overlap as described hereinabove, induces a net 15 transfer of electron density from the catalytic particle to the support matrix **400**. The direction of transfer of electron density is depicted by the arrow. As a result of the wavefunction overlap, the electron density at or near the surface of the catalytic particle **100** has decreased to $Q - \Delta$ where Δ represents the perturbation of electron density at or near the surface of the catalytic particle **100** due to the electronic interaction with the support matrix **400**. The strength of the electronic 20 interaction between the catalytic phase and the electronically active support matrix determines the magnitude of the perturbation Δ in the embodiments shown in Figs. 1B and 1C. A strong electronic interaction reflects significant wavefunction overlap and leads to a greater perturbation

Δ. A weak electronic interaction reflects insignificant wavefunction overlap and leads to a lesser perturbation Δ.

The magnitude of the perturbation of electron density Δ may vary for different particles of a catalytic phase in the instant electronically active supported catalytic materials. Factors that 5 influence Δ include particle size, particle orientation, particle composition, interparticle separation, and support matrix composition. In embodiments of the instant invention having a distribution of particles sizes for the catalytic phase or a plurality of chemically or physically distinct attachment sites on the support matrix for the particles, it is expected that a distribution or range of values of Δ will exist.

10 Perturbations in the electron density at or near the surface of the catalytic phase are not limited solely to perturbations in the magnitude of electron density, but also extend to perturbations in the spatial distribution of electron density at or near the surface of the catalytic phase. In the presence of an inert support matrix, the electron density at or near the surface of a catalytic particle is distributed in a particular, usually inhomogeneous fashion. The electronic 15 interaction of the instant invention may perturb this spatial distribution and may induce a rearrangement, repositioning or otherwise cause a redistribution of electron density at or near the surface of a catalytic particle.

The perturbed electron density and/or spatial distribution thereof leads to modification of the catalytic properties of the catalytic phase. The instant electronic interaction has the effect of 20 extending the catalytically active portion of the instant supported materials beyond the physical boundaries of the catalytic phase. The delocalization of electron density from the catalytic phase to the support matrix, for example, has the effect of enlarging the physical region that influences catalytic behavior to include portions of the support matrix. Rather than being defined solely by

the intrinsic catalytic properties and physical dispersion of the catalytic phase on the support matrix, the instant materials provide for further control and modification of catalytic properties through an electronic interaction mechanism whose origins arise from wavefunction overlap.

One or more catalytic properties pertaining to the performance of supported catalytic

5 materials may be improved through the electronic interaction of the instant materials. These catalytic properties include reaction rate, overall catalytic activity, selectivity, range of catalytically affected reactants, and the range of environmental conditions under which catalytic effects are observed. Overall catalytic activity refers to the rate of reaction and/or the conversion efficiency of a catalyst. Selectivity refers to the ability of a catalyst to discriminate among

10 potential reactants when in the presence of a plurality of reactants. Oftentimes a catalytic reaction is preferentially completed on a particular component within a mixture of components.

Range of catalytically affected reactants refers to the range of chemical species that undergo a catalyzed reaction in the presence of a catalyst. Catalysis of a particular species may become possible through the electronic interaction of the instant materials where said species was not

15 catalyzed by the same catalytic phase supported by an inert support matrix or in the absence of the electronic interaction of the instant catalytic materials. The range of environmental conditions refers to external conditions such as temperature, pressure, concentration, pH, etc.

under which a particular catalytic reaction may occur. The electronic interaction of the instant supported catalyst may facilitate catalytic function at conditions that are more convenient than

20 those for the corresponding reaction in the presence of a conventional supported catalyst showing no electronic interaction. The reaction temperature, for example, may be lowered through use of the instant catalytic materials. Similarly, the catalytic activity at a particular temperature may be greater for a particular reaction through use of the instant electronically

active supported catalytic material. Of particular note in the context of the instant invention is the possibility of inducing a catalytic effect in a catalytic phase where said catalytic phase exhibits no catalytic activity with respect to a particular reaction or process at a particular set of conditions. Electrochemical, chemical, thermal, bond cleavage, bond formation, rearrangements, 5 isomerizations and other types of reactions are within the scope of the instant invention.

As indicated hereinabove, the catalytic phase of the instant supported materials are preferably metals or metal alloys in the form of particles. More preferably, the catalytic particles comprise a transition metal and most preferably the catalytic particles comprise Ni. Transition metals are preferred because their valence electronic structure includes d-orbitals. As previously described 10 by the instant inventor, d-orbitals provide for chemical modification effects through the concept of total interactive environment that lead to novel electronic environments in hydrogen storage materials. Further discussion of the concepts of chemical modification and total interactive environment may be found in the co-pending parent application (U.S. Pat. Appl. Ser. No. 10/405,008) as well as in U.S. Patent Nos. 4,431,561; 4,623,597; 5,840,440; 5,536,591; 15 4,177,473; and 4,177,474 of which the instant inventor is a co-inventor; the disclosures of which are herein incorporated by reference. In the instant invention, the concept of total interactive environment is extended to supported catalytic materials through the electronic interaction between the catalytic phase and support matrix due to wavefunction overlap as described hereinabove. d-orbitals facilitate wavefunction overlap because they are generally spatially well 20 extended and are capable of hybridizing in many ways to achieve a variety of different spatial orientations. Transition metals thereby facilitate the establishment, activation or inducement of the electronic interaction of the instant materials.

- In a typical embodiment of the instant invention, the catalytic particles have a non-uniform particle size distribution and are randomly dispersed spatially on the electronically active support matrix. The range of particle sizes depends on the composition of the catalytic phase as well as the method of preparing and/or dispersing the catalytic particles. Different particle sizes are
- 5 expected to experience different perturbations in the magnitude and/or spatial distribution of electron density at or near the surface of a catalytic particle. A range of perturbations is thus expected for catalytic phases comprising a plurality of catalytic particles that includes a plurality of particle sizes. Dispersion of the catalytic particles refers generally to the spatial distribution of the catalytic particles on the support matrix.
- 10 The support matrix of the instant materials is typically an oxide material. Transition metal oxides (e.g. zirconia, titania), lanthanide oxides (e.g. yttria) and main group oxides (e.g. alumina, silica) are preferred support matrices. Treatment of the surface of the instant support materials (through e.g. etching or passivation) may facilitate the development of electronic interactions between the support materials and a supported catalytic phase.
- 15 The electronic interaction of the instant supported catalytic materials originates from wavefunction overlap between the catalytic phase and the support matrix. The participating wavefunctions may be derived from orbitals that are unoccupied, partially filled or filled and still lead to modification of the electron density at or near the surface of the catalytic phase as described hereinabove. The modification of the electron density of the catalytic phase may result
- 20 in a modification of existing or intrinsic catalytic properties of a catalytic phase (i.e. modification of those catalytic properties of the catalytic phase when unsupported or supported on an inert support matrix) or may result in the establishment of catalytic activity with respect to a particular

reaction at a particular set of conditions where no corresponding activity exists for the catalytic phase when unsupported or supported on an inert support matrix.

EXAMPLE

- An embodiment of a catalyst according to the instant invention is now described. In this
5 example, a supported catalytic material that includes a catalytic phase comprising nickel or nickel alloy particles dispersed on an oxidized metal alloy support is described. The materials of this example are formed from metal alloys represented by the AB, AB₂, AB₅ or A₂B families of hydrogen storage materials where component A is a transition metal, rare earth element or combination thereof and component B is a transition metal element, Al or combination thereof.
10 Representative examples of component A include La, Ce, Pr, Nd, and combinations thereof including mischmetal. Representative examples of component B include Ni, Co, Mn, Al and combinations thereof.

Representative hydrogen storage catalysts having catalytic properties in accordance with the instant invention are disclosed in the parent U.S. Pat. Appl. Ser. No. 10/405,008. For the
15 purposes of this example, we consider catalysis associated with the electrochemical hydrogen storage process. An electrochemical hydrogen storage material produces hydrogen from water through a catalyzed electrochemical reaction and stores the hydrogen for later retrieval. In the retrieval process, stored hydrogen is removed from storage sites and catalytically reacted with hydroxyl ions to form water. During charging of an electrochemical hydrogen storage alloy, a
20 current is provided to the hydrogen storage alloy in the presence of water to form a metal hydride and hydroxyl ions. The alloy is formally reduced in the charging process. The discharging of a metal hydride involves the oxidation of the metal hydride in the presence of hydroxyl ions to

form a metal or metal alloy and water. Electrons are produced during discharging to form a current. The charging and discharging processes are catalyzed.

The alloys of this example were prepared by combining mischmetal and other components in elemental form (purity of each element > 99%) in the required stoichiometric ratio in an MgO crucible. The mischmetal used in this example included La, Ce, Pr, and Nd in a molar ratio of 5 La:Ce:Pr:Nd = 10.5:4.3:0.5:1.4. The total mass of the combined starting elements was approximately 2 kg. The crucible was subsequently placed into a water-cooled induction furnace under a 1 atm. argon atmosphere, heated to about 1350 °C and held at that temperature for 15-20 minutes. During heating, the material in the crucible melted and became superheated to provide 10 better homogeneity. After this heating step, the material was cooled down to just slightly above its melting point (ca. 1280 °C) and immediately poured into a steel mold through a tundish. After pouring, the material was cooled to room temperature. The resulting ingot was then annealed at 950 °C for 8 hours in a vacuum chamber pumped by a diffusion pump. After annealing, the ingot was returned to room temperature. The cooled ingot was then mechanically pulverized and 15 sieved through a 200 mesh filter. The material was further activated to modify surface oxides that form during preparation and improve catalytic performance. Activation is a process in which the surface oxide layer of a hydrogen storage alloy is removed, reduced or modified to improve performance. The process of activation may be accomplished, for example, by etching, electrical forming, pre-conditioning or other methods suitable for removing or altering excess oxides or 20 hydroxides. See, for example, U.S. Pat. No. 4,717,088; the disclosure of which is hereby incorporated by reference.

The activation process facilitates a preferential corrosion of the surface oxide layer to form a porous support matrix with catalytic particles attached thereto. The catalytic particles have sizes

on the order of tens of angstroms and include one or more transition metals. The support matrix is a metal, metal oxide or combination thereof in which the oxidic content may be varied by varying activation conditions. While not wishing to be bound by theory, the instant inventors speculate that as the activation conditions become more extreme and/or activation time becomes 5 sufficiently long, the oxidic content of the support matrix decreases as a preferential corrosion effect converts a greater fraction of the support matrix to the metallic state to form catalytic particles. As corrosion progresses, the support matrix becomes more porous as described in the co-pending parent U.S. Appl. Ser. No. 10/405,008 and in the context of the instant invention, the support matrix is believed by the instant inventors to become more electronically active. As 10 discussed in the co-pending parent U.S. Appl. Ser. No. 10/405,008, preferential corrosion may be facilitated through the inclusion of a microstructure modifying element in the hydrogen storage alloy composition and/or through control of alloy processing conditions.

In this example, the catalytic properties of hydrogen storage alloys in accordance with the instant invention are examined in a low temperature discharge context and compared to a 15 conventional catalytic material lacking an electronic interaction between the catalytic particles and support matrix. More specifically, the specific power of different batteries that include a different hydrogen storage alloy as the negative electrode material was determined at -30 °C. Three UHP C-cell batteries were constructed and tested at -30 °C in an HEV power test. Each C-cell included a nickel hydroxide positive electrode, a separator, a KOH electrolyte and a 20 compacted negative electrode that included a hydrogen storage alloy. One battery included the B1 hydrogen storage alloy ($\text{La}_{10.5}\text{Ce}_{4.3}\text{Pr}_{0.5}\text{Nd}_{1.4}\text{Ni}_{64.5}\text{Co}_{5.0}\text{Mn}_{4.6}\text{Al}_{6.0}\text{Cu}_{3.4}$), a second battery included the B12 hydrogen storage alloy ($\text{La}_{10.5}\text{Ce}_{4.3}\text{Pr}_{0.5}\text{Nd}_{1.4}\text{Ni}_{64.5}\text{Co}_{3.0}\text{Mn}_{4.6}\text{Al}_{6.0}\text{Cu}_{5.4}$), and a third battery included the B hydrogen storage alloy ($\text{La}_{10.5}\text{Ce}_{4.3}\text{Pr}_{0.5}\text{Nd}_{1.4}\text{Ni}_{60.0}\text{Co}_{12.7}\text{Mn}_{5.9}\text{Al}_{4.7}$)

where the B1 and B12 alloys are alloys having catalytic properties according to the instant invention and the B alloy is a conventional alloy that does not benefit from the electronic interaction associated with the materials of the instant invention. The catalytic phase of all three hydrogen storage materials includes catalytic particles comprising nickel or a nickel alloy. The 5 intrinsic catalytic activity of the catalytic particles of the three alloys is expected to be similar. The batteries of this example exemplify NiMH (nickel metal hydride) batteries and are generally representative of rechargeable batteries.

The specific power of each battery was determined in an HEV power test at -30 °C and various states of charge. The HEV power test procedure is discussed in the co-pending parent 10 U.S. Appl. Ser. No. 10/405,008 and the specific power was calculated as the product ($\frac{2}{3}V_{oc}$) ($\frac{1}{3}I_{max}$). Since greater catalytic activity leads to higher specific power, the specific power is used in this example as a measure of the catalytic activity of the three hydrogen storage alloys. Except for the hydrogen storage alloy, the components and configuration of the three batteries were identical.

15 The specific power at a time delay of 6 sec following initiation of a 10 sec 10C discharge pulse of the battery at -30 °C and different states of charge was determined for each of the three batteries at different states of charge (100%, 80%, and 50%). At 100% state of charge, the specific powers of the batteries were determined to be: 260 W/kg (B12), 240 W/kg (B1) and 210 W/kg (B). At 80% state of charge, the specific powers of the batteries were determined to be: 20 210 W/kg (B12), 170 W/kg (B1) and 100 W/kg (B). At 50% state of charge, the specific powers of the batteries were determined to be: 150 W/kg (B12); 105 W/kg (B1) and essentially zero for the B alloy.

The specific power results show that batteries including the two alloys according to the instant invention (B12 and B1) exhibited significantly higher specific powers at all tested states of charge at -30°C than the battery that included the conventional alloy (B). The higher specific powers observed for the B12 and B1 batteries indicate greater catalytic activity and demonstrate

5 a beneficial catalytic effect arising from the electronic interaction described hereinabove for supported catalytic materials according to the instant invention. This example additionally illustrates that supported catalytic materials according to the instant invention provide catalytic activity at conditions at which a conventional supported catalytic material shows no catalytic activity. The electronic interaction present in the B1 and B12 alloys in this example provides for

10 catalytic activity upon discharge at conditions of 50% state of charge and -30 °C, while no catalytic activity was observed in the conventional alloy under the same conditions. Similar degrees of improvement for batteries based on the B1 and B12 alloys relative to a battery based on the B alloy were also observed at room temperature (20 °C) and at 0 °C.

The disclosure and discussion set forth herein is illustrative and not intended to limit the

15 practice of the instant invention. Numerous equivalents and foreseeable variations thereof are envisioned to be within the scope of the instant invention. It is the following claims, including all equivalents, in combination with the foregoing disclosure, which define the scope of the instant invention.